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CONTROL OF IMPURITIES IN THE EPITAXIAL GROWTH OF HIGH
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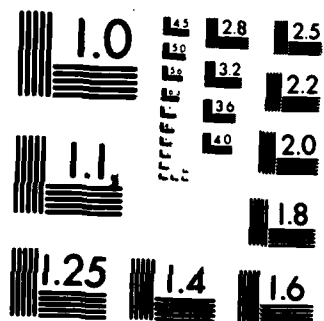
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FINAL REPORT
FOR THE PROGRAM

CONTROL OF IMPURITIES IN THE EPITAXIAL GROWTH
OF HIGH QUALITY GaAs

Contract NO.00014-75-C-0887

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ABSTRACT

— A research program is described on the topic of impurity incorporation during the growth of GaAs epitaxial layers. The major portion of the research was the design, construction, and characterization of a molecular beam mass spectrometry (MBMS) system and its use as a diagnostic analytical tool to evaluate typical gaseous environments used in the growth of III-V single crystal layers. The fundamental gas dynamics of the MBMS sampling process were studied as well as the limitations and correction factors for this technique. Two crystal growth environments were analyzed: a liquid phase epitaxial (LPE) GaAs growth system; and an organometallic vapor phase epitaxy (OMVPE) system. In the former system, it was shown that there are significant concentrations of O, C, and Si gaseous species in the gas ambient which appear to be the major potential impurities. For OMVPE, two topics were emphasized: the side reactions of the organometallic (OM) reactants, particularly those involving oxygen containing species; and the graphite-OM interaction. ← Based on the results of the MBMS study of the LPE GaAs environments, two new deoxygenation methods were developed and were evaluated and compared to the conventional hydrogen deoxygenation method. This evaluation and comparison was made using a solid oxide electrochemical cell method which allows real time in situ measurement of the oxygen activity in the gallium solvent during LPE growth.

I. Introduction

The objective of this program was to develop experimental apparatus and methods for measuring and controlling impurity incorporation in the growth of GaAs layers. More specifically, the research activity developed the techniques of molecular beam mass spectrometry (MBMS) in order to accurately determine the concentration of minor species in the vapor phase under typical conditions of GaAs layer growth. The activities and accomplishments of this program may be classified into four major categories: development of the MBMS technique for analysis of the vapor ambient in crystal growth environments; characterization of the MBMS sampling technique, with emphasis on the correction factors and fundamental limitations; application of MBMS to analyze sources of impurity in typical crystal growth vapor environments; and the development of new crystal growth procedures for GaAs that show promise for reducing impurity levels. Various aspects of these research topics were successively treated in the Ph.D. dissertations by Dr. H. Dun, Dr. D.W. Kisker, and Dr. J.S.C. Chang and are described in several publications. These three individuals are now engaged in research and development on solid state electronic materials at Intel, Bell Labs, and Hewlett Packard, respectively.

This final report will summarize various aspects of the research. Section II is a summary of the development and characterization of the MBMS method, its use in analyzing vapor

ambients typical for the liquid phase epitaxial (LPE) growth of GaAs, and an evaluation of major sources of contamination from typical vapor ambients used in LPE growth. Section III describes the application of the MBMS method in evaluating vapor phase side reactions in the organometallic vapor phase epitaxy (OMVPE) of III-V compounds, a currently attractive method for III-V epitaxial growth. Based on the results of Section II, two new methods for oxygen control during LPE GaAs growth were introduced: chemical gettering; and electro-chemical oxygen pumping. These methods are described in Section IV, along with the results. Section V lists the publications that resulted from this research. Further details on specific aspects of this research are given in these publications.

II. Design and Characterization of a Molecular Beam Mass Spectrometer; Analysis of Impurity Incorporation in Liquid Phase Epitaxial Growth of Gallium Arsenide

The design, construction and characterization of a molecular beam-mass spectrometry system was accomplished in the present research. The system is capable of detecting ppm levels of condensable species, such as water vapor at high temperatures (e.g. 900°C). This technique was successfully applied to the analysis of growth ambient of liquid phase epitaxial gallium arsenide at different temperatures. Major gaseous species detected in the ppm level at the growth temperature range (~890°C) are H₂O, SiO, CO, CH₄, K and oil

vapors. The influence of these species on the purity of the epilayer and the relation to the incorporation of oxygen, silicon, and carbon has been discussed.

The following is a summary of the important features of the operation and design of MBMS.

(i) The following factors distinguish the conical nozzle used in the present study from the sonic nozzle: there is a slower expansion rate; the flow pattern is elongated in the axial direction and contracted in the transverse directions, thus moving the transition from continuous to molecular flow to a point further downstream; there is an increased tendency for cluster formation, and the quenching rate is slower. These factors depend on the geometry in the vicinity of the throat, the background pressure, and the sampling gas characteristics. For the small nozzle orifice and narrow throat channel used in the present study, the viscous effect is significant, as evidenced by the change of the flow patterns for gases of different Reynolds number.

(ii) The mass separation phenomenon, which was shown to be primarily a result of molecular diffusion, gives significant differences between the measured gas composition and the sampled gas composition for gas samples containing species of different masses. When the skimmer is placed in a region free from shock interference and background penetration, the mass separation is found to be approximately proportional to the mass ratio. In order to gain high beam intensity, the skimmer

is positioned as close to the nozzle as possible without encountering significant skimmer interference. This critical position changes as the sampling gas changes.

(iii) The beam modulation technique has advantages for quantitative analysis by minimizing the influence of the background. It is essential for the detection of condensable, reactive and metastable species.

(iv) A broad spectrum of clusters, consisting of both unary and binary species, were observed. As a consequence of a slower expansion rate, the concentration of argon dimer is higher in the present system than for a sonic nozzle.

The analysis of the impurity incorporation in LPE GaAs growth is a complex kinetic process involving such phenomena as vapor transport, gas-solid and gas-liquid catalysis effects, and liquid-solid interface growth kinetics, thus, the contamination levels can not be quantitatively predicted from a simple thermodynamic analysis. However, such an analysis was made to explain general trends. From this analysis, it is shown that oxygen is relatively easily incorporated into the gallium melt but it is difficult for it to occupy an As substitutional site due to its small atomic radius. Carbon, on the other hand, is difficult to dissolve in the melt but once dissolved, is easily incorporated in the growth as an acceptor. Silicon incorporates easily into the melt as well as in the solid and may occupy either a Ga or an As site, thus behaving as an amphoteric impurity. Oxygen is introduced into

the gallium melt during loading and unloading and is rather hard to remove completely because of residual water vapor as well as the slow bulk diffusion rate. Its presence is associated with a donor level. During pregrowth bakeout of the melt in hydrogen, the oxygen activity is reduced and there is a concurrent incorporation of silicon and carbon, which are associated with acceptor levels. This explains the transition from n to p type GaAs with different bakeout conditions.

III. Application of Molecular Beam Mass Spectrometry for the Study of Side Reactions in Organometallic Vapor Phase Epitaxy of III-V Compounds

This phase of the research program has utilized the molecular beam mass spectrometer (MBMS) to study several problems relating to organometallic vapor phase epitaxial (OMVPE) growth of III-V compounds. In particular, the kinetics of the decomposition of trimethylgallium (TMG) as well as the equilibrium interaction of TMG with the impurity species H_2O and O_2 were studied. In addition, the incorporation of O_2 into OMVPE $Al_xGa_{1-x}As$ was studied and its effect upon this material's electrical and optical properties was observed. Finally, the mechanism of one method used to minimize oxygen incorporation in OMVPE $Al_xGa_{1-x}As$ - the use of graphite baffles in the gas stream - was studied by using the MBMS to observe TMA adsorption and desorption transients from graphite, and by using secondary ion mass spectrometry (SIMS) to observe the amount of oxygen in the solid. An adsorption-desorption

model was developed to explain these observations.

The following summarizes the major conclusions of this research program regarding organometallic chemistry:

- i) The theoretical response as a function of mass and temperature of the MBMS was predicted from empirical correlations of quadrupole mass analyzer effects and theoretical treatments of pressure diffusion and free-molecular diffusion effects. The resulting linear T and $m^{5/2} \exp(-m)$ response predicted for concentrations in the low part per million range was tested experimentally using a calibrated mixture of several gases in H_2 at temperatures up to $350^\circ C$. The result was a linear T response up to about $200^\circ C$ and a $m^{2.52} \exp(-m)$ response up to at least mass 129.
- ii) The response of MBMS for H_2O was compared to that of an electronic hygrometer. The MBMS was found to be more linear as well as to have a faster response than the hygrometer, over the range of 0 to 2000 ppm H_2O . The response time of the MBMS was limited by diffusion away from the interface at which a concentration change occurs and the resulting time of transport through the sampling chamber to the sampling nozzle.
- iii) The vapor phase interaction of the oxygen containing compounds D_2O and O_2 with the OM compound TMG was studied. It was found that for low concentrations of oxygen, there is no apparent interaction with TMG. On

the other hand, when H_2O or D_2O is introduced in the presence of TMG, a relatively strong interaction is observed. It was found that a complex forms between D_2O and TMG which is stable at room temperature. By using a xenon internal standard and estimating the mass spectrometer response for the complex using the theoretical mass dependence of the response factors, we were able to obtain an estimate of the equilibrium constant for the complex formation. This value was found to be about 4×10^{-4} with concentrations in ppm.

- vi) Because of the importance of graphite as a construction material in epitaxial reactors, and because there is some indication that its interaction with TMA (trimethyl aluminum) to unusual growth transients during OMVPE, we have studied the adsorption of TMA to graphite using MBMS. By assuming that changes in the transient response of the MBMS were due to adsorption and desorption of TMA to/from graphite, we have obtained an activation energy for the adsorption of TMA to graphite. The value of -15.7 kcal/mole indicates strong adsorption, and also a strong T dependence. In addition, the amount of TMA adsorbed could be estimated from these data and was found to be $3.0 \times 10^{16} \text{ cm}^{-2}$ at 42°C .
- vii) Using the mass 18 isotope of oxygen to intentionally dope OMVPE $Al_xGa_{1-x}As$, we have observed the rapid degradation of optical properties with increasing

$\times 10^2$. In addition, we have compared the oxygen gettering effect of graphite and silicon carbide baffles. The results of SIMS measurements indicated that SiC baffles performed essentially no oxygen gettering. On the other hand oxygen incorporation in solid $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ was greatly reduced when graphite baffles were used. The mechanism of this gettering process can be modeled in terms of adsorption of O_2 to the TMA which is first adsorbed onto the graphite baffles. An estimate of the density of sites available for oxygen adsorption is found to be $1.3 \times 10^{16} \text{ cm}^{-2}$. The excellent agreement between this estimate and the estimate of adsorption site densities from the TMA transient study lends support to this adsorption model of oxygen gettering.

IV. New Methods for Oxygen Control in Liquid Phase Epitaxial Growth of Gallium Arsenide

The results of the study described in section II showed that significant concentrations of O, C, and Si containing species are present in typical vapor environments during LPE GaAs growth. During long time deoxygenation using purified hydrogen - usually for a period of 24 hours - it is likely that C and Si may be incorporated in the Ga solvent and, thus, lead to the incorporation in the GaAs epilayer. The present section describes the use of a solid electrolyte electrochemical cell to monitor the oxygen levels in the Ga solvent and to evaluate

the rate and extent of oxygen removal. In addition to the evaluation of the conventional deoxygenation procedures, two new procedures - chemical deoxygenation and electrochemical pumping - were developed and were evaluated.

Three LPE growth systems are used, namely, the tilt system, the slider system, and the vertical system. The vertical system is a combination of an LPE growth system and an electrochemical cell with the capability of in situ monitoring and control of oxygen in the gallium solvent. An yttria stabilized zirconia tube was employed both as the container for the gallium solvent and as the electrolyte in an oxygen concentration cell. Three methods of deoxygenation of liquid gallium solvent have been investigated, namely, the high temperature anneal in flowing purified hydrogen, the electrochemical coulometric titration, and the use of chemical getters added to the solvent. Properties of the resulting LPE layers have been characterized by the van der Pauw Hall measurement, Schottky barrier technique, deep level transient spectrometry, photoluminescence spectrometry, secondary ion mass spectrometry, and optical and scanning electron microscopy. Semi-insulating Cr doped substrates were used for this study. The Cr concentration in the epilayers has been studied for two growth procedures: the meltback-regrowth procedure and the pregrowth supercooling procedure.

The major conclusions of this research are summarized as follows:

- (1) The layers, which were grown by using the meltback-regrowth method, have high Cr concentration, $2 \times 10^{16} \text{ cm}^{-3}$ versus $5 \times 10^{16} \text{ cm}^{-3}$ in the substrates, whereas the Cr concentration in the layers grown by using the pregrowth supercooling method is $2 \times 10^{15} \text{ cm}^{-3}$. The high Cr concentration in the former case arises from Cr dissolving into the melt during the melt back process and then incorporated in Ga inclusions during the growth process.
- (2) Typical starting conditions in an LPE GaAs system correspond to oxygen levels in the liquid gallium solvent at saturation levels. At 750°C , saturation activity and concentration of oxygen are 10^{13} and 55 ppm, respectively.
- (3) The saturation oxygen activity in Ga-As-O liquid solution is close to the value for a Ga-O binary system, for temperatures in the range of $700\text{--}800^\circ\text{C}$; the presence of 2-3 a/o As apparently does not appreciably alter the thermodynamics of the Ga-O system.
- (4) Annealing the gallium solvent in purified hydrogen at 750°C reduces oxygen activity from 10^{-13} to 10^{-14} over a 20 hour period, for the flow rates of 35 cc/min. The decrease of oxygen activity is consistent with the decrease of free electron density. The rate of decrease of oxygen activity for hydrogen deoxygenation increases with temperature due to enhanced kinetics, whereas the

extent of deoxygenation decreases with increasing temperature. This is consistent with the shift in equilibrium of the deoxygenation reaction: $H_2 + 1/2 O_2 = H_2O$. Increasing hydrogen flow rates increases the rate of deoxygenation only moderately. The rate limiting process is essentially the diffusion of oxygen in the liquid phase.

- (5) Sources of oxygen in the gas are readily detected, leading to higher values of oxygen activity. This technique is thus effective as a monitor for leaks.
- (6) The oxygen level in the liquid gallium solvent may be controlled electrochemically by impressing a voltage between the liquid gallium solvent and the outside of the zirconia tube. With this method, a certain amount of oxygen can be transferred to or from the gallium solvent without direct additions. This technique allows oxygen activity to be varied from 10^{-13} to 10^{-18} at $750^\circ C$. Typically, 1 hour is needed to reduce the oxygen level to the desired level.
- (7) The carrier type is related to the oxygen activity in the gallium solvent; values of oxygen activity below 10^{-16} lead to p-type material. A deep level, 0.707 eV below the conduction band, is detected in the layer grown after electrochemical deoxygenation by the DLTS technique. The oxygen activity in the liquid gallium was 10^{-16} . No direct relation is found between the concentration of this level and the activity of oxygen in the gallium solvent.

- (8) The effective distribution coefficient of oxygen in GaAs LPE growth is about 2.4×10^{-3} at 840°C and $< 1.7 \times 10^{-4}$ at 795°C .
- (9) Use of chemical deoxidizers, such as Ti or Zr, added directly to the gallium melt, provides a rapid and effective deoxygenation. Upon Zr addition to the solvent and after a eight minute incubation period, the oxygen activity value decreases from 10^{-14} to 10^{-18} in about three minutes at 750°C .
- (10) Addition of Zr or Ti lowers the electron density in the resulting LPE layers, and usually produces p-type layers with high mobilities, typically $400 \text{ cm}^2/\text{V-sec}$ at room temperature. The temperature dependence of the p-type mobility shows that there is not a high degree of compensation. No new shallow acceptor levels are found in the Zr or Ti doped layers, judging from the PL spectra. However, in addition to the commonly found deep level (0.904 eV below the conduction band), another level 0.187 eV below the conduction band is found in the Ti doped n-type layer with concentration of 10^{13} cm^{-3} by the DLTS technique. The free hole density in Ti doped p-type layers has a activation energy of 0.64 eV in the temperature range of $400\text{--}500 \text{ K}$. The attempts to measure the deep levels in the Zr doped layers were unsuccessful. The presence of Zr and Ti in the resulting layers is confirmed by the SIMS measurement and Auger spectrometry.

However, no Zr-containing or Ti-containing precipitates are found on the surface of the layers.

- (11) The Zr and Ti additions, especially the Zr additions, increase the fluidity of the gallium solvent and enhance the growth rate, faster growth rate causing a poor surface morphology.
- (12) From the results of the PL spectra, Si and C are found to be the most common shallow acceptor impurities in the LPE GaAs. Both Si and C peaks are present in the layers grown from the slider system and the vertical system. Only Si peaks are present in the layers grown from the tilt system.

V. Publications

Several noteworthy results of this research have been published in the open literature and are listed below. These articles provide specific detailed information on the topics specified by the respective titles.

A. Papers published:

1. "The Gas Dynamics of a Conical Nozzle Molecular Beam Sampling System", Chemical Physics 38, 161 (1979), (H. Dun, B. L. Mattes and D. A. Stevenson).
2. "Molecular Beam Sampling for Mass Spectrometry", The UTI Journal, 2, 1-3 (1979), (D. A. Stevenson).
3. "Molecular Beam Sampling for Mass Spectrometric Studies of Chemical Vapor Deposition Environments", Proceedings of the Seventh International Conference on Chemical Vapor Deposition, T. O. Sedgwick and H. Lydtin, Eds., The Electrochemical Society, Proceedings, 79-3, 530-540 (1979) (D. Kisker, H. Dun and D. A. Stevenson).
4. "In Situ Analysis of Minor Gaseous Species in Crystal Growth Ambients Using Molecular Beam Mass Spectrometry", 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, J.W. Hastie, ed., pgs. 411-428 (1979) (H. Dun, B.L. Mattes and D. A. Stevenson).
5. "Observations on Binary Clusters Formed Upon Expansion of Argon Mixtures", Chem. Physics 52, 469-479, (1980) (H. Dun and D. A. Stevenson).
6. "The Influence of Ti and Zr Additions on GaAs Liquid Phase Epitaxial Growth", Applied Physics Letters, 37 (9), 832-834 (1980) (D. A. Stevenson, P.I. Ketrush, S.C. Chang, and A. Borschevsky).
7. "Analysis of Water Vapor in Purified Gas Systems", Semiconductor Measurement Technology; NBS Special Publication 400-69 pgs. 143-152; H.A. Schafft, S. Ruthberg and E.C. Cohen eds. (1981) (H. Dun, B.L. Mattes and D. A. Stevenson).
8. "Molecular Beam Mass Spectrometry Studies of Vapor Phase Reactions of Organometallic Compounds", Chemical Vapor Deposition pp. 212-226, J.M. Blocher and G.E. Vuillard, eds., The Electrochemical Society 1981 (D.W. Kisker and D. A. Stevenson).

9. "Analysis of Correction Factors Used for Molecular Beam MassSpectrometry", Proceedings, 30th Annual Conference on Mass Spectrometry and Allied Topics pg. 702, F.W. Lampe, Ed. American Society for Mass Spectrometry 1982 (D.W. Kisker and D. A. Stevenson).
10. "Mechanism of Graphite Baffle Gettering in Organometallic Vapor Phase Epitaxy; Adsorption of Trimethylaluminum on Graphite", Journal of Electronic Materials, 12, No. 2, 459 (1983) (D.W. Kisker and D. A. Stevenson).
11. "The Vapor Phase Interaction of Trimethylaluminum With Graphite During OMVPE", Journal de Physique 43, C5-221 (1982) (with D.W. Kisker, J.N. Miller, G.B. Stringfellow and D. A. Stevenson).

B. Patents Issued

1. "Method for Controlling Impurities in Liquid Phase Epitaxial Growth", United States Patent Number 4,371,420 (Feb. 1, 1983). D. A. Stevenson.
2. "Electrochemical Deoxygenation for Liquid Phase Epitaxial Growth: United States Patent Number 4,389,274 (June 21, 1983). D. A. Stevenson.

C. Papers Accepted for Publication

1. "In Situ Electrochemical Monitoring and Control of Oxygen in Liquid Phase Epitaxial Growth of GaAs", J. Crystal Growth (S.C. Chang, G.Y. Meng and D. A. Stevenson), in press.
2. "The Control and In-Situ Monitoring of Oxygen in Liquid Phase Gallium Arsenide Growth," Proceedings, High Temperature Materials Chemistry Symposium, May 1983, (S.C. Chang and D. A. Stevenson).

D. Ph.D. Dissertations

1. "In Situ Analysis Using Molecular Beam-Mass Spectrometry-Application to Crystal Growth," H. Dun.
2. "The Study of Side Reactions During Organometallic Vapor Phase Epitaxy of III-V Compounds," D.W. Kisker.
3. "Measurement and Control of Oxygen in Liquid Phase Epitaxial Growth of GaAs," J.S-C Chang.